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(54) ANTIMICROBIAL FILM AND ITS PRODUCTION

(57) Abstract:

PURPOSE: To produce an antimicrobial film excellent in adhesion, durability, heat-sealing properties and barrier properties and useful for food wrap, etc., by applying radioactive rays to the surface of a polymer base material for graft polymerization of acrylic acid, immersing it in a silver ion-containing solution and making the silver ions adsorbed thereon.

CONSTITUTION: The antimicrobial film is obtained by applying radioactive rays such as electron beams to one or both the sides of a polymer base material such as PE for graft polymerization of acrylic acid, immersing it in a silver ion-containing solution such as a silver nitrate solution and making the silver ions adsorbed thereon.

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* NOTICES *
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3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The antibacterial film which has the complex ion which stuck at least to one side of a macromolecule base material at the graft polymerization layer and this graft polymerization layer of an acrylic acid.
[Claim 2] The manufacture approach of an antibacterial film according to claim 1 of having the process which performs radiation irradiation at least on one side of a macromolecule base material, the process which carries out the graft polymerization of the acrylic acid, and the process which immerses and sticks to the solution containing complex ion.
[Claim 3] The manufacture approach of the antibacterial film according to claim 2 characterized by performing to coincidence the process of radiation irradiation, and the process which carries out the graft polymerization of the acrylic acid.
[Claim 4] The manufacture approach of the antibacterial film according to claim 2 characterized by performing the process which carries out the graft polymerization of the acrylic acid after the process of radiation irradiation.
[Claim 5] The manufacture approach of the antibacterial film according to claim 2 characterized by performing adsorption of complex ion after an alkaline solution neutralizes the graft layer of an acrylic acid.
[Claim 6] The manufacture approach of the antibacterial film according to claim 2 characterized by that the amount of radiation irradiation to a macromolecule base material constructs a bridge in the macromolecule which forms this macromolecule base material irradiating more than the amount of slack radiation irradiation.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the antibacterial film used for food packing, a building material, etc. or an antibacterial cast, and its manufacture approach.
[0002]
[Description of the Prior Art] Making various macromolecule base materials, such as a food wrapping material, clothing, sanitary goods, kitchen utensils, a water treating unit, and a filter, contain an antibacterial substance, the technique which controls growth of a harmful microorganism had been existing from before. In the case of a food wrapping material, usually, a complex ion permutation zeolite is especially used as main antibacterial substances from the safety to human being. In a metal ion, antibacterial [of complex ion] is the strongest, and especially a silver nitrate solution has the history long used for medical application, the object for midwives, and military affairs as a germicide.
[0003] When antibacterial [of complex ion] is measured in a culture medium, checking growth of a microorganism completely by 1 or the concentration of 10 ppm is known, and it is known for underwater [without a nutrient] that the order of 10ppb also has the effectiveness of the growth inhibition to a

microorganism (T. Sugio, Agric.Biol.Chem., 1981 [45, 2037,]). Although the antibacterial device is not clear completely, complex ion is actively incorporated to the inside of the body of a microorganism, it reacts to an enzyme and a selection target, and it is said that enzyme inhibition is started as a result. As a result, antibacterial [of complex ion] has little singularity, and bacteria, yeast, and receiving molding and checking growth almost equally are known.

[0004] In order to carry out long duration continuation not only of a food wrapping material but antibacterial, it is necessary to fix the complex ion which has antibacterial in a macromolecule base material. But although it is the approach of immobilization of simple complex ion making water soluble polymers, such as casein and gelatin, distributing complex ion, and applying on the macromolecule base material aiming at this solution, drying, and obtaining an antibacterial surface layer, there are many problems -- the adhesive stability of a water soluble polymer layer and the water soluble polymer layer itself become ****-ization to a microorganism. It is the silver permutation zeolite to which the approach generally conventionally used as the fixed approach permutes and creates about 5% of the sodium ion of a zeolite with complex ion. This silver permutation zeolite is scoured by 1 thru/or 3% of concentration in plastics, and growth of a microorganism is checked according to an operation of the complex ion eluted slightly or the silver permutation zeolite which contacts a microorganism directly. Thus, it is in the point how the need point in an antibacterial film can supply [how] complex ion efficiently to the ambient atmosphere (solid phase, the liquid phase, or gaseous phase) containing the microorganism which will contact a film if complex ion is efficiently put in another way to a microorganism.

[0005]

[Problem(s) to be Solved by the Invention] However, in the scour lump by the PURASUTCHIKU sheet of a silver permutation zeolite like before, the complex ion which will be used even if it laminates only the inside of a molding container with a silver permutation zeolite kneading lump sheet is only a part for very few silver permutation zeolites exposed to a front face, and the molding of a complicated configuration had constraint that the approach of a surface lamination could not be used, either. This shows that the use effectiveness of expensive silver is very low. If an antibacterial sheet is furthermore used in the condition that there is a nutrition source of supply, since antibacterial is decided by competition relation of the growth stopping power of a microorganism and the growth rate of a microorganism by complex ion, it needs to increase the absolute magnitude of the complex ion which can contact a microorganism. However, the former scoured, by the crowded method, 5% of the content of the barrier nature fall by continuation productivity and the pinhole etc. to a zeolite is an upper limit in a weight ratio, and the complex ion concentration on the front face of a film had the problem that it was changed only in the range restricted very much. Therefore, in order that the trouble which should solve this invention may raise the use effectiveness of complex ion, the complex ion fixed bed with high adhesive property and endurance is created by the graft-ized reaction only in the front face of a macromolecule base material, and according to use, adjustment of complex ion concentration is possible, and it is in offering the technique which creates an antibacterial macromolecule base material applicable also to a complicated cast with practical reinforcement.

[0006]

[Means for Solving the Problem] this invention person came to find out the following approaches, as a result of studying wholeheartedly a means to solve the above troubles. That is, it is invention of the antibacterial film characterized by having prepared the graft polymerization layer of an acrylic acid at least in one side of a macromolecule base material by the radiation irradiation method, and for the alkaline solution having neutralized this acrylic-acid graft layer preferably, and next making complex ion stick to this graft polymerization layer. Either the so-called preoperative irradiation method or the coincidence irradiating method is OK as how to prepare the acrylic-acid graft layer by the radiation irradiation method. Moreover, the radiation irradiation graft-ized approach of making a graft-

ized location limiting only to the front face of a macromolecule base material is also effective in obtaining the antibacterial film of this invention by performing slack radiation irradiation making this macromolecule base material construct a bridge over a macromolecule base material beforehand, and making an acrylic-acid monomer and a graft reaction perform to the appropriate back.

[0007] Let slack radiation irradiation be a standard here making a bridge construct so that you may become 40% or more with a gel molar fraction about a macromolecule base material "for it to be slack radiation irradiation to making a macromolecule base material construct a bridge." Although the amount of radiation irradiation required at a gel molar fraction to become 40% or more changes with classes of giant molecule, 8 or more Mrads are sufficient with low density polyethylene, and the electron beam irradiation of 12 or more Mrads is typically sufficient for it with high density polyethylene. In addition, also economically the radiation irradiation of 128 or more Mrads is inefficient-like, and since the mechanical strength of a macromolecule base material may also fall, it is not desirable. This invention is described in a detail below.

[0008] The graft-ized reaction to a macromolecule base material itself has desirable radiation irradiation, such as an electron ray and a gamma ray, from a practical standpoint, although it can start with many means, such as radiation irradiation (an electron ray, gamma ray), an optical exposure, plasma treatment, corona treatment, and frame processing. While its reaction is quick since the graft-ized reaction by such radiation irradiation is a high dose rate, and there is the advantage in which can perform an exposure at low temperature and the amount of grafts is large, the greatest merit is the point [radiation irradiation] that prior sterilization of a macromolecule base material is possible. Moreover, after reaction termination is the point important detrimentally in a graft layer, when the point in which a graft is possible also contacts especially food, without using the polymerization initiator in which the decomposition product of an offensive odor remains in reaction initiation. Although the approach (the coincidence irradiating method) of making the monomer which should be graft-ized coexist with a macromolecule base material at the graft-ized reaction by radiation irradiation, and carrying out radiation irradiation to coincidence is efficient, since a monomer independent polymerization is not avoided, it is effective only when the homopolymerization object of a monomer does not bar the operation (antibacterial, mechanical property). By the approach (preoperative irradiation method) of irradiating a radiation and making it reacting only to a macromolecule base material with a monomer beforehand as the graft-ized approach by other radiation irradiation at the appropriate back, although homopolymerization of the above-mentioned monomer can be controlled, reactivity falls.

[0009] Although a reaction starts the graft reaction generally performed by radiation irradiation with the radical kind generated inside a giant-molecule base material, you may think that the concentration of the generated radical kind is proportional to a radiation exposure. In the amount of radiation irradiation low like bridge formation of a macromolecule base material can be disregarded, the rate of a graft in fixed reaction time is proportional to the amount of radiation irradiation mostly, the rate of a graft also increases as reaction time increases, and a graft layer advances toward the interior from the front face of a macromolecule base material. You may conclude that the increment in the rate of a graft is proportional to reduction of the thickness of an unreacted macromoleoule base material mostly. Although the solvent which does not dissolve and swell a base material must be used for obtaining a graft ghost, with the mechanical strength of a macromolecule base material maintained, reaction time must be shortened and advance inside [of a graft layer] a macromolecule base material must be stopped on the way, in this case, there are few amounts of the monomer which carries out a graft to a macromolecule base material front face, the rate of a graft becomes small, and there is dilemma that metal adsorption capacity falls. On the other hand, when a macromolecule base material performs radiation irradiation which is sufficient for constructing

a bridge, the graft layer of advance inside is comparatively late, and it grows up towards the bulk side of a monomer solution rather. That is, it becomes possible to carry out localization of the graft part to the front face of a macromolecule base material.

[0010] Giant-molecule base materials here are radiation bridge formation mold resin or copolymerization resin, such as polyethylene, polypropylene, polystyrene, the poly methyl pentene -1, polysulfone, polyacrylate, polyacrylamide, polyvinyl chloride, a polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, and a polyvinyl pyrrolidone, and in the case of radioactive decay mold polymers, such as a polyisobutylene and poly vinylidene chloride, the same vinyl mold monomer also needs to reduce the amount of radiation irradiation extremely, and needs to make it react to it. Since these distinction is influenced by the conditions at the time of radiation irradiation (temperature, ambient atmosphere), according to conditions, not only polyolefin resin but nylon, poly dimethylsiloxane, and Teflon can use them. The gestalt of these giant-molecule base materials will not interfere fundamentally, if even radiation irradiation can do them no matter the shape of the shape of the shape of the shape of tabular, a cylinder, and a sheet and a film, fibrous, and a bead, powder, and a hollow filament, a cast, etc. may be what configurations.

[0011] As an electron ray property, an acceleration electron ray and a gamma ray may be especially desirable, and any, such as for example, an electro curtain system, a scanning type, a doubles canning type, a BANDE graph, and a cold cathode, are [the field of penetrating power and activation effectiveness to acceleration voltage may be at least 10 or more Kvs, and] sufficient as especially a radiation here as an electron ray accelerator. It can measure with the gel molar fraction using the solvent which may dissolve this macromolecule base material simple [bridge formation of a macromolecule base material here]. In addition, in order to cause deactivation of graft active species (mainly free radical) on the occasion of radiation irradiation if an oxygen density is high, or to cause collapse of the polymer by oxidation reaction, it is desirable to perform the permutation by inert gas, such as nitrogen and helium, and to aim at an oxygen density fall. However, it is not this limitation when using a peroxide as graft active species.

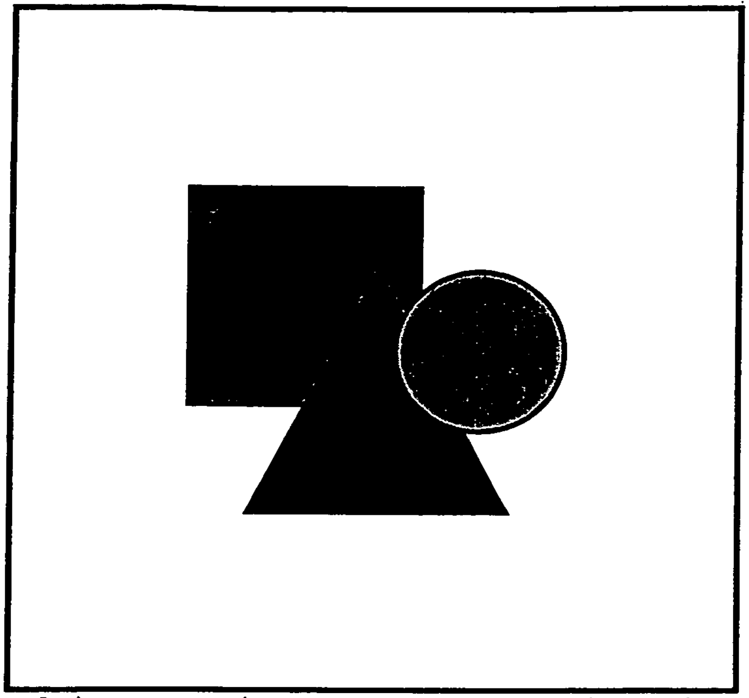
[0012] A graft-ized reaction can be attained after radiation irradiation by making it react with the monomer which was made to react using a monomer, direct, or a solvent, or was made to evaporate. Generally, since it is common for a reaction rate to be slow, the reaction in the solution system using a solvent is [a monomer independent] advantageous. A radical polymerization inhibitor like Mohr's salt, a redox system additive like metal copper or the 1st copper chloride, and polymerization inhibitor like the hydroquinone monomethyl ether may be used together in order to prevent a monomer independent gay polymerization. Adsorption of the complex ion in a graft layer is easily attained by immersing a graft object into the solution containing complex ion, for example, a silver nitrate solution. 25-mol % of a carboxyl group reacts with complex ion only by adsorption being immersed in the silver nitrate solution of 5mM(s) for about 1 hour. The complex ion rate of adsorption of the graft object which neutralized the acrylic-acid graft object with the sodium-hydroxide solution etc. is still quicker, it reacts by the immersion for 15 minutes, and 77-mol % of a carboxyl group reacts 57% in 1 hour. It is possible to control adsorption complex ion concentration by concentration adjustment of a silver nitrate solution, immersion time amount, and immersion temperature with a natural thing, when high-concentration complex ion is not required in this way.

[0013]

[Function] This invention can adsorb complex ion to the reactive site of the carboxyl group which adsorbs complex ion by the radiation irradiation graft-ized reaction efficiently by the ion-exchange nature with a carboxyl group high [that it can localize on a front face very much] of a giant-molecule base material. In the approach of this invention, it localizes, and it is efficient on a front face and antibacterial high complex ion can be used for it.

[0014]

[Example] Hereafter, although an example explains this invention in detail, the contents of this invention are not restricted to an example.
Electron beam irradiation was carried out so that it might become the absorbed dose of 4Mrad(s) with the electron-beam-irradiation equipment (the product made from ESI, 175/15/20, 50 ppm or less of oxygen densities, acceleration voltage 150kv) which permuted the semi-gross density polyethylene film (consistency 0.928g/cm3) with an example 1 thickness of 100 micrometers with nitrogen gas. The irradiated polyethylene film contacted only one side in 50% acrylic-acid water solution beforehand deaerated by nitrogen inert gas replacement, and it performed the reaction for 2 minutes at 70 degrees C, continuing nitrogen aeration. The graft-ized polyethylene film was quickly thrown in in the methanol of an overlarge, suspended the reaction, and rinsed succeedingly. The rate of a graft was calculated by the gravimetry after the vacuum drying at 50 degrees C. The rate of a graft was 2.5%. After rinsing, it was immersed in the silver nitrate solution of the concentration of 5mM, the ion exchange was performed, and the amount of complex ion permutations was computed from concentration change of a silver nitrate solution. Immersion time amount to a silver nitrate solution was set as for 1 minute, 2.5 minutes, and 5 minutes at the room temperature. The complex ion permutation sample was cut by the microtome after a vacuum drying, and measured the film internal division blanket-like voice of a silver atom by the scanning electron microscope and the X-ray microanalyser. Apart from the graft reaction, as a result of collecting after putting the polyethylene sample which carried out electron beam irradiation on the same conditions into the glass filter and flowing back in toluene after a gravimetry for 48 hours, performing a gravimetry again and asking for a gel molar fraction, it is 0%, and the bridge formation by electron beam irradiation had not taken place. Count of a gel molar fraction is based on the following formulas.
Gel molar fraction =100x(weight after solvent extraction)/(weight before solvent extraction)
[0015] After performing graft-ization by the same actuation as example 2 example 1 and calculating the rate of a graft, it was immersed in the sodium-hydroxide solution 1% for 1 hour, and the graft layer was neutralized, after rinsing, it was immersed in the silver nitrate solution of the concentration of 5mM for 5 minutes, and the ion exchange was performed. Next actuation was performed like the example 1.
[0016] Electron beam irradiation was carried out so that it might become the absorbed dose of 4Mrad(s) with the electron-beam-irradiation equipment (the product made from ESI, 175/15/20, 50 ppm or less of oxygen densities, acceleration voltage 150kv) which performed corona treatment to the semi-gross density polyethylene film same with having used for example 3 example 1, applied 50% acrylic acid beforehand deaerated by nitrogen inert gas replacement, and 3% JIAKURIROKISHI pentaerythritol water solution at 70 degrees C, and was permuted with nitrogen gas. After treatment of the graft-ized polyethylene film was performed like the example 1, and immersion time amount to a silver nitrate was set as for 5 minutes. The rate of a graft was 2.8% with the acrylic-acid base.
[0017] Electron beam irradiation of 32Mrad(s) was performed to the semi-gross density polyethylene film same with having used for example 4 example 1, and the graft reaction was performed by the same approach as an example 1. Reaction time was set as for 4 minutes. The rate of a graft after performing the same after treatment as an example 1 was 2.5%. Immersion time amount to a silver nitrate solution was set as for 5 minutes. As a result of collecting after putting the polyethylene sample which carried out electron beam irradiation on the same conditions apart from the graft reaction into the glass filter and flowing back in toluene after a gravimetry for 48 hours, performing a gravimetry again and asking for a gel molar fraction, it is 66%, and the bridge formation by electron beam irradiation had arisen.
[0018] The zeolite which permuted 15 mol % of the sodium of examples of a comparison with complex ion was mixed with the medium-density-polyethylene pellet (consistency 0.928 g/cm3) so that it might become 2% by the weight ratio, and the film with a thickness of 100 micrometers was obtained with the



melting extrusion process. The obtained film was cut by the microtome and the film internal division blanket-like voice of a silver atom was measured by the scanning electron microscope and the X-ray microanalyser.

[0019] a result -- an example -- setting -- a sample -- the cutting plane was clearly divided into three layers, and distribution of a silver atom was two-layer [of both front faces] (graft layer). Distribution of the silver atom in a graft layer is almost uniform, and the difference by the depth in a graft layer was seen [in / no / the sample]. The cutting plane of the sample by the example 1 of a comparison is very uniform, and, as for the difference in the depth direction, distribution of a silver atom was not seen, either. The result of an example and the example of a comparison is collectively indicated to Table 1. In addition, it searched for reinforcement and metal adsorbent by the approach shown below the formula showing count of surface silver concentration below, respectively whenever [rate of graft, and silver atom diffusion].

Rate of graft =100x(weight before weight-graft after graft)/(weight before a graft)

Whenever [silver atom diffusion] = 100-100x(film thickness of layer in which silver atom does not exist)/(film thickness before a reaction)

Surface silver concentration: What expressed with the unit of mu mol / m2, and mum the concentration of the silver atom per [which exists by the depth of 1 micrometer of front faces of a film] unit area.

[0020]

[Table 1]

[0021]

[Effect of the Invention] According to this invention, the thing of a film made for a front face to carry out localization of the location where a silver atom exists very much is possible so that clearly also from the result of whenever [silver atom diffusion / of Table 1]. According to this invention, since advance of a graft layer advances toward the interior of a film from a film front face, also whenever [large diffusion] can manufacture also whenever [smaller than this value diffusion]. When the film which constructed the bridge especially by electron beam irradiation is used for a reaction, a graft location is unevenly distributed in a pole front face, and effective in localization of complex ion.

[0022] On the other hand, by the approach of the example of a comparison, the silver atom is diffused throughout a film and the silver atom in the interior

is not contributed to antibacterial at all. In the case of a conventional method, a zeolite scours the surface concentration of a silver atom and it can take only a very small value from constraint of whenever [permutation / of a lump content and complex ion], but Since whenever [carrying-out / distribute a graft part on a front face to the order of a molecular level, and / only to a pole front face /-in depth direction-localization and complex ion permutation] is changed in the very large range (0 thru/or 70%) by the approach of this invention, Surface silver concentration can be adjusted in the large range, and the upper limit has hundreds possible times of the upper limit of a conventional method. Since existence of a graft layer is restricted to the pole front face of a film, when using as a film, the antibacterial film which inherited the property of the film used as raw materials, such as heat-sealing nature, a lamination adhesive property, and barrier nature, as it was is obtained reflecting the mechanical strength of the film of original also in reinforcement. Moreover, it is in ** for it to be able to apply also not only to the materials in which this approach has two-dimensional breadth like a film from the transparency property of a radiation but to a three-dimension-cast.

TECHNICAL FIELD

[Industrial Application] This invention relates to the antibacterial film used for food packing, a building material, etc. or an antibacterial cast, and its manufacture approach.

PRIOR ART

[Description of the Prior Art] Making various macromolecule base materials, such as a food wrapping material, clothing, sanitary goods, kitchen utensils, a water treating unit, and a filter, contain an antibacterial substance, the technique which controls growth of a harmful microorganism had been existing from before. In the case of a food wrapping material, usually, a complex ion permutation zeolite is especially used as main antibacterial substances from the safety to human being. In a metal ion, antibacterial [of complex ion] is the strongest, and especially a silver nitrate solution has the history long used for medical application, the object for midwives, and military affairs as a germicide.
[0003] When antibacterial [of complex ion] is measured in a culture medium, checking growth of a microorganism completely by 1 or the concentration of 10 ppm is known, and it is known for underwater [without a nutrient] that the order of 10ppb also has the effectiveness of the growth inhibition to a microorganism (T. Sugio, Agric.Biol.Chem., 1981 [45, 2037,]). Although the antibacterial device is not clear completely, complex ion is actively incorporated to the inside of the body of a microorganism, it reacts to an enzyme and a selection target, and it is said that enzyme inhibition is started as a result. As a result, antibacterial [of complex ion] has little singularity, and bacteria, yeast, and receiving molding and checking growth almost equally are known.
[0004] In order to carry out long duration continuation not only of a food wrapping material but antibacterial, it is necessary to fix the complex ion which has antibacterial in a macromolecule base material. But although it is the approach of immobilization of simple complex ion making water soluble polymers, such as casein and gelatin, distributing complex ion, and applying on the macromolecule base material aiming at this solution, drying, and obtaining an antibacterial surface layer, there are many problems -- the adhesive stability of a water soluble polymer layer and the water soluble polymer layer itself become ****-ization to a microorganism. It is the silver permutation zeolite to which the approach generally conventionally used as the fixed approach permutes and creates about 5% of the sodium ion of a zeolite with complex ion. This silver permutation zeolite is scoured by 1 thru/or 3% of concentration in plastics, and growth of a microorganism is checked according to an operation of the complex ion eluted slightly or the silver permutation zeolite which contacts a microorganism directly. Thus, it

is in the point how the need point in an antibacterial film can supply [how] complex ion efficiently to the ambient atmosphere (solid phase, the liquid phase, or gaseous phase) containing the microorganism which will contact a film if complex ion is efficiently put in another way to a microorganism.

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the thing of a film made for a front face to carry out localization of the location where a silver atom exists very much is possible so that clearly also from the result of whenever [silver atom diffusion / of Table 1]. According to this invention, since advance of a graft layer advances toward the interior of a film from a film front face, also whenever [large diffusion] can manufacture also whenever [smaller than this value diffusion]. When the film which constructed the bridge especially by electron beam irradiation is used for a reaction, a graft location is unevenly distributed in a pole front face, and effective in localization of complex ion.
[0022] On the other hand, by the approach of the example of a comparison, the silver atom is diffused throughout a film and the silver atom in the interior is not contributed to antibacterial at all. In the case of a conventional method, a zeolite scours the surface concentration of a silver atom and it can take only a very small value from constraint of whenever [permutation / of a lump content and complex ion], but Since whenever [carrying-out / distribute a graft part on a front face to the order of a molecular level, and / only to a pole front face /-in depth direction-localization and complex ion permutation] is changed in the very large range (0 thru/or 70%) by the approach of this invention, Surface silver concentration can be adjusted in the large range, and the upper limit has hundreds possible times of the upper limit of a conventional method. Since existence of a graft layer is restricted to the pole front face of a film, when using as a film, the antibacterial film which inherited the property of the film used as raw materials, such as heat-sealing nature, a lamination adhesive property, and barrier nature, as it was is obtained reflecting the mechanical strength of the film of original also in reinforcement. Moreover, it is in ** for it to be able to apply also not only to the materials in which this approach has two-dimensional breadth like a film from the transparency property of a radiation but to a three-dimension-cast.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in the scour lump by the PURASUTCHIKU sheet of a silver permutation zeolite like before, the complex ion which will be used even if it laminates only the inside of a molding container with a silver permutation zeolite kneading lump sheet is only a part for very few silver permutation zeolites exposed to a front face, and the molding of a complicated configuration had constraint that the approach of a surface lamination could not be used, either. This shows that the use effectiveness of expensive silver is very low. If an antibacterial sheet is furthermore used in the condition that there is a nutrition source of supply, since antibacterial is decided by competition relation of the growth stopping power of a microorganism and the growth rate of a microorganism by complex ion, it needs to increase the absolute magnitude of the complex ion which can contact a microorganism. However, the former scoured, by the crowded method, 5% of the content of the barrier nature fall by continuation productivity and the pinhole etc. to a zeolite is an upper limit in a weight ratio, and the complex ion concentration on the front face of a film had the problem that it was changed only in the range restricted very much. Therefore, in order that the trouble which should solve this invention may raise the use effectiveness of complex ion, the complex ion fixed bed with high adhesive property and endurance is created by the graft-ized reaction only in the front face of a macromolecule base material, and according to use, adjustment of complex ion concentration is possible, and it is in offering the technique which creates an antibacterial macromolecule base material applicable also to a complicated

cast with practical reinforcement.

MEANS

[Means for Solving the Problem] this invention person came to find out the following approaches, as a result of studying wholeheartedly a means to solve the above troubles. That is, it is invention of the antibacterial film characterized by having prepared the graft polymerization layer of an acrylic acid at least in one side of a macromolecule base material by the radiation irradiation method, and for the alkaline solution having neutralized this acrylic-acid graft layer preferably, and next making complex ion stick to this graft polymerization layer. Either the so-called preoperative irradiation method or the coincidence irradiating method is OK as how to prepare the acrylic-acid graft layer by the radiation irradiation method. Moreover, the radiation irradiation graft-ized approach of making a graft-ized location limiting only to the front face of a macromolecule base material is also effective in obtaining the antibacterial film of this invention by performing slack radiation irradiation making this macromolecule base material construct a bridge over a macromolecule base material beforehand, and making an acrylic-acid monomer and a graft reaction perform to the appropriate back.
[0007] Let slack radiation irradiation be a standard here making a bridge construct so that you may become 40% or more with a gel molar fraction about a macromolecule base material "for it to be slack radiation irradiation to making a macromolecule base material construct a bridge." Although the amount of radiation irradiation required at a gel molar fraction to become 40% or more changes with classes of giant molecule, 8 or more Mrads are sufficient with low density polyethylene, and the electron beam irradiation of 12 or more Mrads is typically sufficient for it with high density polyethylene. In addition, also economically the radiation irradiation of 128 or more Mrads is inefficient-like, and since the mechanical strength of a macromolecule base material may also fall, it is not desirable. This invention is described in a detail below.
[0008] The graft-ized reaction to a macromolecule base material itself has desirable radiation irradiation, such as an electron ray and a gamma ray, from a practical standpoint, although it can start with many means, such as radiation irradiation (an electron ray, gamma ray), an optical exposure, plasma treatment, corona treatment, and frame processing. While its reaction is quick since the graft-ized reaction by such radiation irradiation is a high dose rate, and there is the advantage in which can perform an exposure at low temperature and the amount of grafts is large, the greatest merit is the point [radiation irradiation] that prior sterilization of a macromolecule base material is possible. Moreover, after reaction termination is the point important detrimentally in a graft layer, when the point in which a graft is possible also contacts especially food, without using the polymerization initiator in which the decomposition product of an offensive odor remains in reaction initiation. Although the approach (the coincidence irradiating method) of making the monomer which should be graft-ized coexist with a macromolecule base material at the graft-ized reaction by radiation irradiation, and carrying out radiation irradiation to coincidence is efficient, since a monomer independent polymerization is not avoided, it is effective only when the homopolymerization object of a monomer does not bar the operation (antibacterial, mechanical property). By the approach (preoperative irradiation method) of irradiating a radiation and making it reacting only to a macromolecule base material with a monomer beforehand as the graft-ized approach by other radiation irradiation at the appropriate back, although homopolymerization of the above-mentioned monomer can be controlled, reactivity falls.
[0009] Although a reaction starts the graft reaction generally performed by radiation irradiation with the radical kind generated inside a giant-molecule base material, you may think that the concentration of the generated radical kind is proportional to a radiation exposure. In the amount of radiation

irradiation low like bridge formation of a macromolecule base material can be disregarded, the rate of a graft in fixed reaction time is proportional to the amount of radiation irradiation mostly, the rate of a graft also increases as reaction time increases, and a graft layer advances toward the interior from the front face of a macromolecule base material. You may conclude that the increment in the rate of a graft is proportional to reduction of the thickness of an unreacted macromolecule base material mostly. Although the solvent which does not dissolve and swell a base material must be used for obtaining a graft ghost, with the mechanical strength of a macromolecule base material maintained, reaction time must be shortened and advance inside [of a graft layer] a macromolecule base material must be stopped on the way, in this case, there are few amounts of the monomer which carries out a graft to a macromolecule base material front face, the rate of a graft becomes small, and there is dilemma that metal adsorption capacity falls. On the other hand, when a macromolecule base material performs radiation irradiation which is sufficient for constructing a bridge, the graft layer of advance inside is comparatively late, and it grows up towards the bulk side of a monomer solution rather. That is, it becomes possible to carry out localization of the graft part to the front face of a macromolecule base material.

[0010] Giant-molecule base materials here are radiation bridge formation mold resin or copolymerization resin, such as polyethylene, polypropylene, polystyrene, the poly methyl pentene -1, polysulfone, polyacrylate, polyacrylamide, polyvinyl chloride, a polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, and a polyvinyl pyrrolidone, and in the case of radioactive decay mold polymers, such as a polyisobutylene and poly vinylidene chloride, the same vinyl mold monomer also needs to reduce the amount of radiation irradiation extremely, and needs to make it react to it. Since these distinction is influenced by the conditions at the time of radiation irradiation (temperature, ambient atmosphere), according to conditions, not only polyolefin resin but nylon, poly dimethylsiloxane, and Teflon can use them. The gestalt of these giant-molecule base materials will not interfere fundamentally, if even radiation irradiation can do them no matter the shape of the shape of the shape of the shape of tabular, a cylinder, and a sheet and a film, fibrous, and a bead, powder, and a hollow filament, a cast, etc. may be what configurations.

[0011] As an electron ray property, an acceleration electron ray and a gamma ray may be especially desirable, and any, such as for example, an electro curtain system, a scanning type, a doubles canning type, a BANDE graph, and a cold cathode, are [the field of penetrating power and activation effectiveness to acceleration voltage may be at least 10 or more Kvs, and] sufficient as especially a radiation here as an electron ray accelerator. It can measure with the gel molar fraction using the solvent which may dissolve this macromolecule base material simple [bridge formation of a macromolecule base material here]. In addition, in order to cause deactivation of graft active species (mainly free radical) on the occasion of radiation irradiation if an oxygen density is high, or to cause collapse of the polymer by oxidation reaction, it is desirable to perform the permutation by inert gas, such as nitrogen and helium, and to aim at an oxygen density fall. However, it is not this limitation when using a peroxide as graft active species.

[0012] A graft-ized reaction can be attained after radiation irradiation by making it react with the monomer which was made to react using a monomer, direct, or a solvent, or was made to evaporate. Generally, since it is common for a reaction rate to be slow, the reaction in the solution system using a solvent is [a monomer independent] advantageous. A radical polymerization inhibitor like Mohr's salt, a redox system additive like metal copper or the 1st copper chloride, and polymerization inhibitor like the hydroquinone monomethyl ether may be used together in order to prevent a monomer independent gay polymerization. Adsorption of the complex ion in a graft layer is easily attained by immersing a graft object into the solution containing complex ion, for example, a silver nitrate solution. 25-mol % of a carboxyl group reacts with complex ion only by adsorption being immersed in the silver nitrate solution of 5mM(s) for about 1 hour. The complex ion rate

of adsorption of the graft object which neutralized the acrylic-acid graft object with the sodium-hydroxide solution etc. is still quicker, it reacts by the immersion for 15 minutes, and 77-mol % of a carboxyl group reacts 57% in 1 hour. It is possible to control adsorption complex ion concentration by concentration adjustment of a silver nitrate solution, immersion time amount, and immersion temperature with a natural thing, when high-concentration complex ion is not required in this way.

OPERATION

[Function] This invention can adsorb complex ion to the reactive site of the carboxyl group which adsorbs complex ion by the radiation irradiation graft-ized reaction efficiently by the ion-exchange nature with a carboxyl group high [that it can localize on a front face very much] of a giant-molecule base material. In the approach of this invention, it localizes, and it is efficient on a front face and antibacterial high complex ion can be used for it.

EXAMPLE

[Example] Hereafter, although an example explains this invention in detail, the contents of this invention are not restricted to an example.
Electron beam irradiation was carried out so that it might become the absorbed dose of 4Mrad(s) with the electron-beam-irradiation equipment (the product made from ESI, 175/15/20, 50 ppm or less of oxygen densities, acceleration voltage 150kv) which permuted the semi-gross density polyethylene film (consistency 0.928g/cm3) with an example 1 thickness of 100 micrometers with nitrogen gas. The irradiated polyethylene film contacted only one side in 50% acrylic-acid water solution beforehand deaerated by nitrogen inert gas replacement, and it performed the reaction for 2 minutes at 70 degrees C, continuing nitrogen aeration. The graft-ized polyethylene film was quickly thrown in in the methanol of an overlarge, suspended the reaction, and rinsed succeedingly. The rate of a graft was calculated by the gravimetry after the vacuum drying at 50 degrees C. The rate of a graft was 2.5%. After rinsing, it was immersed in the silver nitrate solution of the concentration of 5mM, the ion exchange was performed, and the amount of complex ion permutations was computed from concentration change of a silver nitrate solution. Immersion time amount to a silver nitrate solution was set as for 1 minute, 2.5 minutes, and 5 minutes at the room temperature. The complex ion permutation sample was cut by the microtome after a vacuum drying, and measured the film internal division blanket-like voice of a silver atom by the scanning electron microscope and the X-ray microanalyser. Apart from the graft reaction, as a result of collecting after putting the polyethylene sample which carried out electron beam irradiation on the same conditions into the glass filter and flowing back in toluene after a gravimetry for 48 hours, performing a gravimetry again and asking for a gel molar fraction, it is 0%, and the bridge formation by electron beam irradiation had not taken place. Count of a gel molar fraction is based on the following formulas.
Gel molar fraction =100x(weight after solvent extraction)/(weight before solvent extraction)
[0015] After performing graft-ization by the same actuation as example 2 example 1 and calculating the rate of a graft, it was immersed in the sodium-hydroxide solution 1% for 1 hour, and the graft layer was neutralized, after rinsing, it was immersed in the silver nitrate solution of the concentration of 5mM for 5 minutes, and the ion exchange was performed. Next actuation was performed like the example 1.
[0016] Electron beam irradiation was carried out so that it might become the absorbed dose of 4Mrad(s) with the electron-beam-irradiation equipment (the product made from ESI, 175/15/20, 50 ppm or less of oxygen densities, acceleration voltage 150kv) which performed corona treatment to the semi-gross density polyethylene film same with having used for example 3 example

1, applied 50% acrylic acid beforehand deaerated by nitrogen inert gas replacement, and 3% JIAKURIROKISHI pentaerythritol water solution at 70 degrees C, and was permuted with nitrogen gas. After treatment of the graft-ized polyethylene film was performed like the example 1, and immersion time amount to a silver nitrate was set as for 5 minutes. The rate of a graft was 2.8% with the acrylic-acid base.

[0017] Electron beam irradiation of 32Mrad(s) was performed to the semi-gross density polyethylene film same with having used for example 4 example 1, and the graft reaction was performed by the same approach as an example 1. Reaction time was set as for 4 minutes. The rate of a graft after performing the same after treatment as an example 1 was 2.5%. Immersion time amount to a silver nitrate solution was set as for 5 minutes. As a result of collecting after putting the polyethylene sample which carried out electron beam irradiation on the same conditions apart from the graft reaction into the glass filter and flowing back in toluene after a gravimetry for 48 hours, performing a gravimetry again and asking for a gel molar fraction, it is 66%, and the bridge formation by electron beam irradiation had arisen.

[0018] The zeolite which permuted 15 mol % of the sodium of examples of a comparison with complex ion was mixed with the medium-density-polyethylene pellet (consistency 0.928 g/cm3) so that it might become 2% by the weight ratio, and the film with a thickness of 100 micrometers was obtained with the melting extrusion process. The obtained film was cut by the microtome and the film internal division blanket-like voice of a silver atom was measured by the scanning electron microscope and the X-ray microanalyser.

[0019] a result -- an example -- setting -- a sample -- the cutting plane was clearly divided into three layers, and distribution of a silver atom was two-layer [of both front faces] (graft layer). Distribution of the silver atom in a graft layer is almost uniform, and the difference by the depth in a graft layer was seen [in / no / the sample]. The cutting plane of the sample by the example 1 of a comparison is very uniform, and, as for the difference in the depth direction, distribution of a silver atom was not seen, either. The result of an example and the example of a comparison is collectively indicated to Table 1. In addition, it searched for reinforcement and metal adsorbent by the approach shown below the formula showing count of surface silver concentration below, respectively whenever [rate of graft, and silver atom diffusion].

Rate of graft =100x(weight before weight-graft after graft)/(weight before a graft)

Whenever [silver atom diffusion] = 100-100x(film thickness of layer in which silver atom does not exist)/(film thickness before a reaction)

Surface silver concentration: What expressed with the unit of mu mol / m2, and mum the concentration of the silver atom per [which exists by the depth of 1 micrometer of front faces of a film] unit area.

[0020]

[Table 1]